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STUDIES OF NON-RESONANT CHARGE TRANSFER
BETWEEN ATOMIC IONS AND ATOMS

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Pittsburgh University

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BY

R. JOHNSEN, M. T. LEU AND MANFRED A. BIONDI

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Studies of Non-Resonant Charge Transfer between Atomic Ions and Atoms²

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Abstract

Measurements of non-resonant charge transfer between atomic ions and atoms have been made in a drift tube/mass spectrometer apparatus as a function of E/p (drift field/gas pressure) at 295 K. At $E/p = 0$ the charge transfer coefficients are: $k(\text{He}^+, \text{Hg}) = (1.6 \pm 0.3) \times 10^{-9} \text{ cm}^3/\text{sec}$, $k(\text{Ar}^+, \text{Hg}) = (1.5 \pm 0.3) \times 10^{-11}$, $k(\text{Kr}^+, \text{Hg}) = (8.5 \pm 2) \times 10^{-12}$. For $\text{Ne}^+ + \text{Hg}$ and $\text{Xe}^+ + \text{Hg}$ k is $\leq 10^{-12}$, while for $\text{He}^+ + \text{Ne}$ and $\text{He}^+ + \text{Ar}$ k is $\leq 10^{-13} \text{ cm}^3/\text{sec}$. Little dependence of $k(\text{He}^+, \text{Hg})$ and $k(\text{Ar}^+, \text{Hg})$ on ion energy is found up to mean energies of $\sim 0.25 \text{ eV}$. Comparison of the measured rates with available theories suggests an inability to predict the moderately slow reaction rates.

I. INTRODUCTION

The process of symmetrical, resonant charge transfer between atomic ions and atoms,



is rather well understood, with theoretical predictions in satisfactory agreement with experimental measurements on many ion-atom systems for energies ranging from thermal (~ 300 K) to many keV.¹ In contrast, the non-resonant and accidentally resonant asymmetrical charge transfer processes,



are less well understood, with substantial disagreement between the observed and theoretically predicted behaviors at low energies.

For example, given the energy defect $\Delta\epsilon(\infty)$, i.e. the energy difference between the initial and final states of reaction (2) with the particles at infinite separation, the "adiabatic criterion" introduced by Massey² leads to prediction of a small charge transfer rate at collision velocities smaller than

$$v_{\max} = a \Delta\epsilon(\infty) / h \quad , \quad (3)$$

where a is a "collision distance" (empirically $\sim 7\text{\AA}$) and h is Planck's constant. This "uncertainty principle" statement that only violent collisions can blur the energy states sufficiently to cause a transfer between initial and final states has apparently been violated by the finding of a number of cases where, in spite of appreciable energy defects, the charge transfer rates at thermal energies are fast.³

The application to asymmetrical charge transfer of the method of estimating ion-molecule reaction rates proposed by Gioumouisis and

Stevenson⁴ for systems where point charge-induced dipole (polarizable atom or molecule) forces dominate also has not been particularly successful. According to this model, for impact parameters less than a certain value the induced dipole interaction leads to inward spiralling orbits⁵ (until the short-range repulsive interaction between ion and atoms is encountered), leading to sufficient time for a reaction to take place. In applying this model to charge transfer at low energies, Rapp and Francis⁶ assumed that all collisions with impact parameters smaller than this critical value would lead to charge transfer about half of the time, while those with larger impact parameters would have negligible probability of charge transfer. As we shall see, experimental observations bear no apparent relationship to this simple picture of low energy charge transfer rates; in some cases rates approaching the Gioumousis and Stevenson prediction are found, in others, the rates are orders of magnitude smaller.

Recently, a more logical description of the thermal energy charge transfer process has been given by Turner-Smith et al.³ In this model, the principal long range ion-molecule interaction is again induced dipole, and the Langevin criterion⁵ is again used to determine the critical impact parameter for spiralling. Here, however, the probability of occurrence of asymmetrical charge transfer is calculated from the net transition rate at the curve crossing between initial ($A^+ + B$) and final ($A + B^+$) energy states of the system as the particles spiral in past the crossing point and then out again. The transition rate in turn is determined by the particles' relative velocity at the crossing and the steepness of the crossing [which depends on $\Delta\epsilon(\infty)$ and the difference in polarizability of A and B]. We shall return to a discussion of this model after we present our experimental results.

In order to gain an insight into the non-resonant charge transfer process at low energies we have studied the systems $\text{He}^+ + \text{Hg}$, $\text{Ne}^+ + \text{Hg}$, $\text{Ar}^+ + \text{Hg}$, $\text{Kr}^+ + \text{Hg}$, $\text{Xe}^+ + \text{Hg}$, $\text{He}^+ + \text{Ne}$, and $\text{He}^+ + \text{Ar}$. In the following sections we briefly describe the method of measurement, present our determinations of the charge transfer rates for the various reactions over the energy range from thermal (295 K) to 0.34 eV, and compare our results with the predictions of the theory of Turner-Smith et al.

II. APPARATUS AND METHOD OF MEASUREMENT

The drift mobility tube/mass spectrometer apparatus shown in Fig. 1 has been described in detail previously.⁷⁻⁹ Generation of the parent ions [A^+ in reaction (2)] in the ion source is accomplished by pulsed electron bombardment of the parent gas (typically at a pressure of ~ 0.1 to 0.8 Torr). In the cases of krypton and xenon the parent gas is mixed with a comparable amount of argon buffer gas before being admitted to the ion source. A fraction of the ions in the pulse are admitted through a 0.4 cm diam injection orifice into the drift region where they move under the action of a uniform axial electric field established by means of a series of guard rings.

In the cases where the reactant gas [B in reaction (2)] is mercury, the desired vapor pressure in the drift region is established by evaporation from a temperature controlled drop of mercury contained in a stainless steel side arm connected to the ion source by a large conductance vacuum valve. (It was not possible to connect the side-arm directly to the drift region.) The reactant gas pressure in the drift space is measured by means of a Baratron[®] pressure gauge located in the vacuum system adjacent to the drift tube. These measurements are made before adding and after removing the parent (and buffer) gas to the tube

via the ion source, and the reactant concentration determinations are corrected for the "sweep-out" effect produced by the addition of the parent gas.⁷

A fraction of the parent ions which do not undergo charge transfer or diffuse away from the drift tube axis effuse through the 0.046 cm diam exit orifice into the differentially pumped quadrupole mass spectrometer where they are mass-selected. Arriving ions are counted by means of the channeltron electron multiplier whose output pulses are sent to a multichannel analyzer operating in a time-of-flight mode.

The charge transfer rate coefficients are determined by the "additional residence time" method which has been described in detail elsewhere.^{7,8} In this technique, the residence time of a pulse of ions in the drift tube (i.e., the time the ions can undergo charge transfer with the reactant gas) is varied by subjecting the ions to a programmed sequence of drift fields, either stopping them (thermal energy measurements) or reversing their motion (higher energy measurements) for a controlled time interval. By measuring the loss of parent ions as a function of the additional residence time in the drift (reaction) space and correcting for ion loss by lateral diffusion one can determine the charge transfer rate. Studies have been carried out as a function of ion energy by varying the ratio of the drift field to gas pressure E/p .

The ions' mean energy $\bar{\epsilon}_{ion}$ has been calculated using the formula derived by Wannier¹⁰ assuming a constant mean free time between ion-atom collisions. In this model, the ions' mean energy is related to their drift velocity through the expression,

$$\bar{\epsilon}_{ion} = 3/2 kT + 1/2(M+m) v_d^2, \quad (4)$$

where m is the mass of the ion, M the mass of the atom (buffer gas), and v_d the measured drift velocity of the ion. As noted previously,⁷ in the case of ions drifting in their parent gas (where long-range, resonant charge transfer between ion and atom is of importance), this formula may overestimate the ions' energy by as much as a factor $4/\pi$ at high E/p . However, since the reactions under study exhibit little dependence on ion energy, the approximate energy scale obtained by use of Wannier's formula without correction is sufficiently accurate for our purposes.

III. RESULTS

Charge transfer rate coefficients (or upper limits thereof) were obtained for He^+ , Ne^+ , Ar^+ , Kr^+ and Xe^+ ions colliding with Hg atoms and for He^+ ions colliding with Ne and Ar atoms.

A. Charge Transfer to Hg Atoms

The measured charge transfer coefficients for $\text{He}^+ + \text{Hg}$ are shown as a function of E/p in Fig. 2. These measurements were carried out at a mercury vapor density $[\text{Hg}] = 8 \times 10^{12} \text{ cm}^{-3}$ and an ambient temperature $T = 295 \text{ K}$. The rate coefficient at thermal energy ($E/p = 0$) is $k(\text{He}^+, \text{Hg}) = 1.6 \times 10^{-9} \text{ cm}^3/\text{sec}$ and falls slowly with increasing ion energy to a value of $\sim 9 \times 10^{-10} \text{ cm}^3/\text{sec}$ at $\bar{\epsilon}_{\text{ion}} = 0.24 \text{ eV}$ ($E/p = 45 \text{ V-cm}^{-1} \text{ Torr}^{-1}$ in helium).

In the case of $\text{Ne}^+ + \text{Hg}$ no charge transfer reaction was detected over the range, $295 \text{ K} < \bar{\epsilon}_{\text{ion}} < 0.15 \text{ eV}$ ($0 < E/p < 40$ in neon), even when the mercury vapor density was increased to $[\text{Hg}] \sim 7 \times 10^{13} \text{ cm}^{-3}$. From these observations we can set a limit for the charge transfer rate coefficient, $k(\text{Ne}^+, \text{Hg}) \lesssim 10^{-12} \text{ cm}^3/\text{sec}$.

The data for the charge transfer reaction $\text{Ar}^+ + \text{Hg}$ are shown in Fig. 3. The mercury vapor density was $[\text{Hg}] = 6.8 \times 10^{13} \text{ cm}^{-3}$ and the gas temperature $T = 295 \text{ K}$. The thermal energy ($E/p = 0$) point shown, $k(\text{Ar}^+, \text{Hg}) = 1.5 \times 10^{-11} \text{ cm}^3/\text{sec}$, represents the average of 20 data points which exhibited an rms deviation of 10% about this value. No simple variation of the rate coefficient is noted with ion energy over the range, $295 \text{ K} < \bar{\epsilon}_{\text{ion}} < 0.34 \text{ eV}$ ($0 < E/p < 117$ in argon); a constant value of k provides an acceptable fit to the data over this range.

The charge transfer reaction $\text{Kr}^+ + \text{Hg}$ was found to have a rate coefficient $k(\text{Kr}^+, \text{Hg}) = 8.5 \times 10^{-12} \text{ cm}^3/\text{sec}$ at thermal (295 K) energy. No measurements as a function of E/p were obtained in this case.

No detectable charge transfer by the reaction $\text{Xe}^+ + \text{Hg}$ was observed at 295 K and $E/p = 0$ at a mercury vapor concentration $[\text{Hg}] \sim 7 \times 10^{13} \text{ cm}^{-3}$, setting a limit on the rate coefficient of $k(\text{Xe}^+, \text{Hg}) \lesssim 10^{-12} \text{ cm}^3/\text{sec}$.

B. Charge Transfer of He^+ with Ne and Ar

In these measurements the reactant gas density was increased to rather large values, $\sim 3 \times 10^{15} \text{ cm}^{-3}$, yet no charge transfer was observed to take place at 295 K and $E/p = 0$. From these observations we can set a limit for both $k(\text{He}^+, \text{Ne})$ and $k(\text{He}^+, \text{Ar})$ of $\lesssim 10^{-13} \text{ cm}^3/\text{sec}$.

IV. DISCUSSION AND CONCLUSIONS

The principal uncertainties in the values of the charge transfer rate coefficients arise from imperfect knowledge of the mercury vapor density in the drift space. The Baratron pressure measuring system has an accuracy of $\pm 10\%$ at the pressures used ($\sim 3 \times 10^{-4}$ to $\sim 2 \times 10^{-3}$ Torr). All other sources of error in the rate coefficient determinations

are smaller than this; therefore we assign an overall uncertainty of approximately $\pm 20\%$ to the measured values of k .

The results of our measurements are summarized in Table I. The observation of moderate to fast rates in a number of cases strongly suggests that the charge transfer process under study is one which leaves the product ion in an electronically excited state, i.e.,



otherwise the energy defects $\Delta\epsilon(\infty)$ of the reactions would be large (> 1 eV) and the thermal energy transfer rates small.

In arriving at the values of k_{th} given in Table I, Eqs. (16) and (17) of the paper by Turner-Smith et al. (TS), applicable in cases where the polarizability of reactant atom B is much larger than that of parent atom A, were used. This approximation should be valid except in the case of $Xe^+ + Hg$, since the values of the atomic polarizability α for He, Ne, Ar, Kr, Xe and Hg are,¹¹ respectively, 0.22, 0.35, ~ 2 , 2.5, 4.5, and 9.8 \AA^3 .

The quantity $\Delta\epsilon(\infty)$ also enters the theory, with small values favoring a large reaction rate. We have calculated the several small positive energy defects for various excited levels of B^{+*} using tabulated energy level values.¹² The relevant values of $\Delta\epsilon(\infty)$ are: (He, Hg) 0.27, 0.37, 0.41, 0.44, 0.61, 0.64 eV; (Ne, Hg) 0.45, 0.61, 0.69 eV; (Ar, Hg) 0.93, 5.3 eV; (Kr, Hg) 3.6 eV; (Xe, Hg) 1.7 eV; (He, Ne) 3.0 eV; (He, Ar) 8.8 eV. These values have been used in the theoretical formula to calculate the contribution of each of the important curve crossings and the results summed to obtain the estimates of k_{th} given in Table I.

It will be seen from Table I that the TS theory is successful in predicting the large $He^+ + Hg$ charge transfer coefficient. (This value

is remarkably close to the charge transfer rate of $1.5 \times 10^{-9} \text{ cm}^3/\text{sec}$ calculated on the assumption that half of the collisions which result in spiralling orbits also lead to charge transfer.) The TS theory is also consistent with our failure to observe charge transfer for the systems (Ne^+, Hg) , (Xe^+, Hg) , (He^+, Ne) and (He^+, Ar) . However, the theory fails to predict the observation of a charge transfer coefficient of $\sim 10^{-11} \text{ cm}^3/\text{sec}$ in the cases of (Ar^+, Hg) and (Kr^+, Hg) .

It appears possible to understand the successes and failures of the TS theory in terms of the limitations imposed by its basic assumptions. The theory follows the Landau-Zener approach of estimating the net transition rate at the pseudo-crossing of the adiabatic potential curves of initial $(A^+ + B)$ and final $(A + B^{+*})$ states of the same species (i.e. same symmetry properties). Turner-Smith et al. use an empirical formula given by Olson et al.¹³ for H_{12} , the matrix element of the interaction Hamiltonian, to calculate the net transition rate. This formula was derived from an analysis of experimental and theoretical charge transfer and ion-ion recombination data, assuming that only large separation pseudo-crossings between two states of the same species were of importance in the processes under study. The charge transfer reaction between He^+ and Hg, with small $\Delta\epsilon(\infty)$ values and a very large difference in the polarizabilities of He and Hg, probably fits this case well, so the theory is successful in predicting the observed magnitude of the transfer rate.

In other cases, such as $\text{Ar}^+ + \text{Hg}$ and $\text{Kr}^+ + \text{Hg}$, where smaller but measurable rates of charge transfer are observed, the minimum energy defects are substantially larger and the differences in polarizabilities somewhat smaller. In these cases the TS theory predicts extremely small

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charge transfer rates because it ignores (a) contributions from true crossings of the potential curves of states of different symmetry properties and (b) contributions at inner pseudo-crossings (in the molecular region). Both of these contributions to charge transfer are normally smaller than that due to an outer crossing in a favorable case; states of different symmetry properties require coupling between the electronic and nuclear motions to permit a transition to take place at the crossing, while the small transition rate at an inner crossing is normally overshadowed by transitions at a favorable outer crossing. Inclusion of these additional effects in the theory of non-resonant charge transfer may well lead to more accurate predictions of the slow charge transfer reaction rates.

The observed decrease of $k(\text{He}^+, \text{Hg})$ with increasing ion energy (see Fig. 2) does not follow the predictions of theory. Both the simple Langevin spiralling theory⁵ and the modification by Turner-Smith *et al.*³ yield rate coefficients which are independent of ion energy. However, the additional factors which should be included in a more complete theory (see previous paragraph) may lead to a slight modification of the predicted energy dependence. The apparent lack of dependence of $k(\text{Ar}^+, \text{Hg})$ on ion energy (see Fig. 3) is, however, in keeping with the predictions of the simpler theories.

It is clear from the present results that the "adiabatic criterion,"² which has had some success in predicting charge transfer at moderate energies,¹ fails completely at low energies in cases such as (He^+, Hg) , (Ar^+, Hg) and (Kr^+, Hg) . From the energy defects for these reactions, one calculates from Eq. (3) that v_{max} , the velocity below which the charge transfer cross section Q_{tr} should decrease radically, is in

excess of 4×10^6 cm/sec. Our measurements refer to near-thermal ions with velocities of $\sim 2 \times 10^5$ cm/sec and smaller; thus, the observation of fast charge transfer ($Q_{tr} > 10^{-14}$ cm²) at thermal energies for $\text{He}^+ + \text{Hg}$ is in direct contradiction to the adiabatic criterion. Even the more modest thermal energy charge transfer rates for $\text{Ar}^+ + \text{Hg}$ and $\text{Kr}^+ + \text{Hg}$ ($Q_{tr} \sim 5 \times 10^{-16}$ cm²) are inconsistent with the adiabatic hypothesis, because in these cases the ratio of $v_{\text{max}}/v_{\text{thermal}}$ is even larger, the order of 50, and one therefore should expect vanishingly small charge transfer rates.

The present results, which have revealed very large and not well understood variations in the rates of charge transfer between atomic ions and atoms for different systems, are of interest for laser applications. Given a sufficiently fast rate of charge transfer leading to formation of the product ion in an excited state, the necessary population inversion for laser action becomes possible. This mechanism has been invoked to account for the emitted lines in several helium - metal vapor lasers.¹⁴⁻¹⁶

The very fast $\text{He}^+ + \text{Hg}$ charge transfer process evidently produces excited states of Hg^+ ; however, with the very small ion currents used in our drift tube it does not seem feasible to determine which states are formed by detecting the optical radiation emitted. Therefore, we are considering continuing these studies in a flowing afterglow system³ where the ion densities can be made considerably higher, and thus detectable optical signals should be produced.

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Note added

Very recently, Bardsley and Sinha (private communication) have examined the sensitivity of the TS theory's predictions to variations in the value of the empirically determined interaction Hamiltonian. They find that for quite reasonable changes in the Hamiltonian (in view of the scatter in the data used for the empirical determination) the predicted charge transfer coefficients change by many orders of magnitude, casting serious doubt on the quantitative aspects of the present form of the TS theory.

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TABLE I. Comparison of measured and predicted charge transfer rate coefficients at thermal (295 K) energy.

Reaction	$k_{\text{exp}} (\text{cm}^3/\text{sec})^{\text{a}}$	$k_{\text{th}} (\text{cm}^3/\text{sec})^{\text{b}}$
$\text{He}^+ + \text{Hg}$	$(1.6 \pm 0.3) \times 10^{-9}$	1.6×10^{-9}
$\text{Ne}^+ + \text{Hg}$	$\lesssim 10^{-12}$	$\sim 10^{-14}$
$\text{Ar}^+ + \text{Hg}$	$(1.5 \pm 0.3) \times 10^{-11}$	$\sim 10^{-43}$
$\text{Kr}^+ + \text{Hg}$	$(8.5 \pm 2) \times 10^{-12}$	~ 0
$\text{Xe}^+ + \text{Hg}$	$\lesssim 10^{-12}$	$\sim 10^{-80}$
$\text{He}^+ + \text{Ne}$	$\lesssim 10^{-13}$	$\sim 10^{-45}$
$\text{He}^+ + \text{Ar}$	$\lesssim 10^{-13}$	$\sim 10^{-16}$

^a present experiment.

^b calculated from Ref. 3 (see text for details).

FIGURE CAPTIONS

- Fig. 1. Simplified diagram of the drift mobility tube/mass spectrometer apparatus (approximately to scale).
- Fig. 2. The $\text{He}^+ + \text{Hg}$ charge transfer coefficient as a function of E/p and $\bar{\epsilon}_{\text{ion}}$ at $T = 295 \text{ K}$. The mercury vapor concentration is $[\text{Hg}] = 8 \times 10^{12} \text{ cm}^{-3}$.
- Fig. 3. The $\text{Ar}^+ + \text{Hg}$ charge transfer coefficient at $T = 295 \text{ K}$ and $[\text{Hg}] = 6.8 \times 10^{13} \text{ cm}^{-3}$. The point at $E/p = 0$ represents the average of 20 data points which exhibit a $\pm 10\%$ rms deviation from this value.

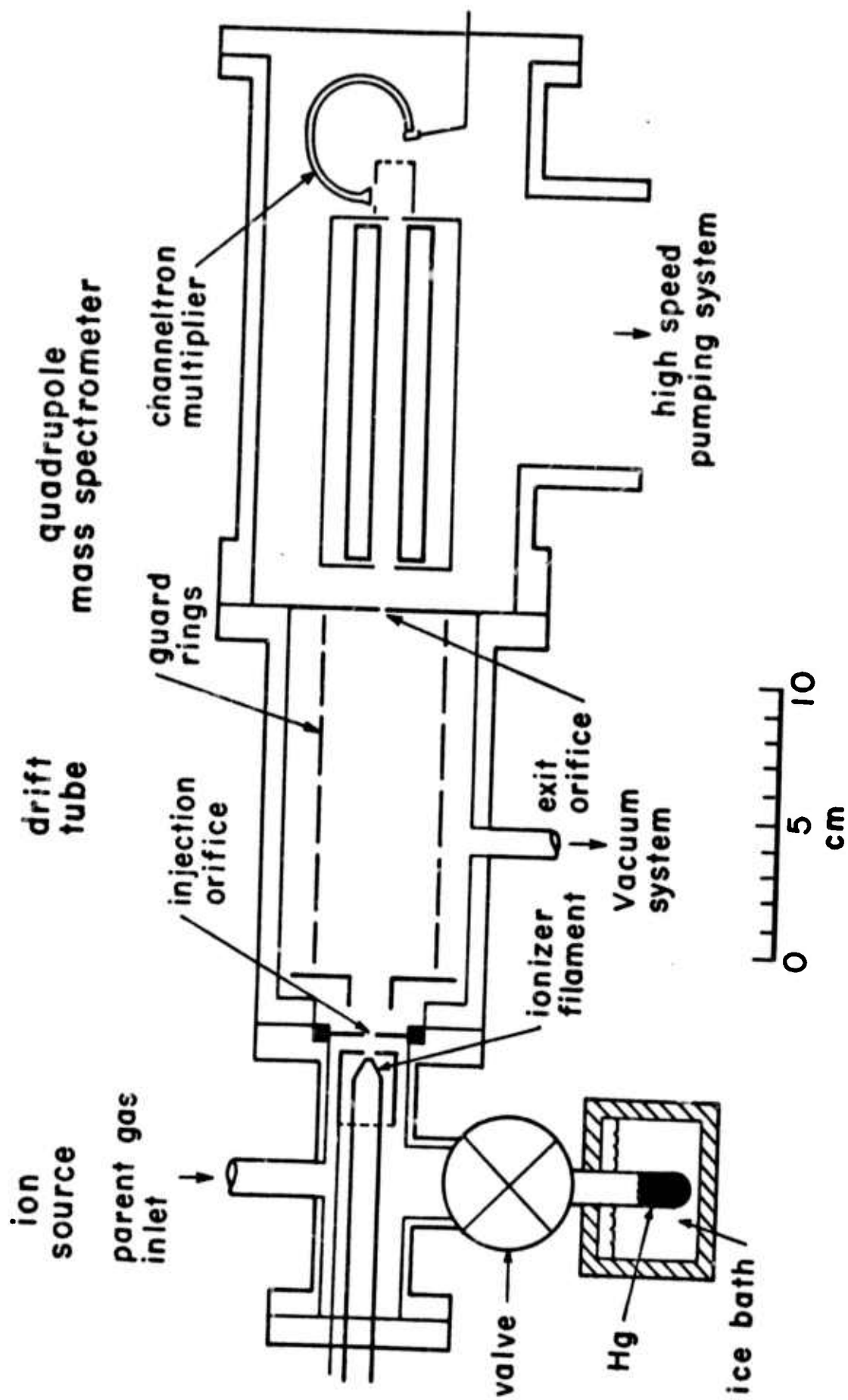


Figure 1

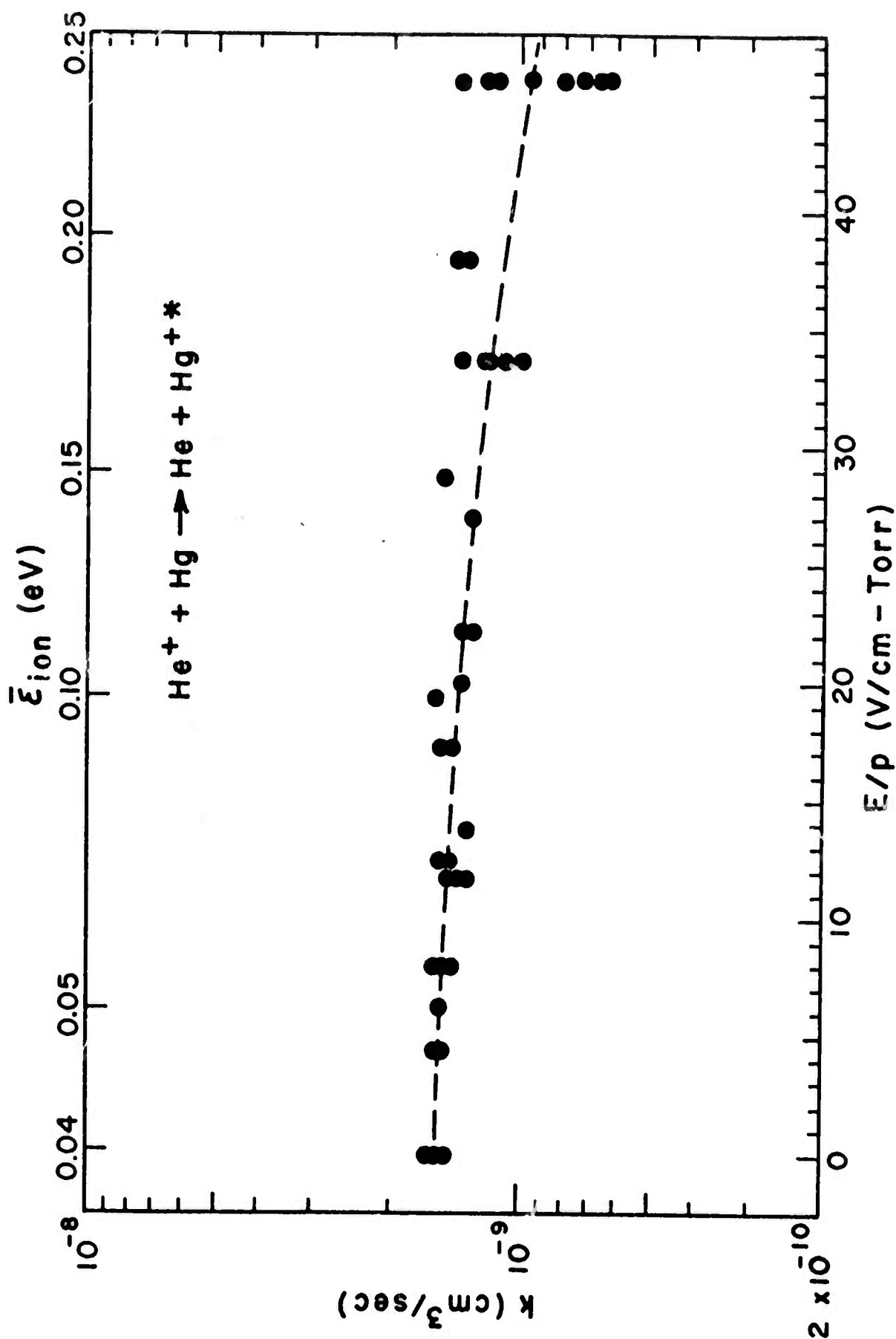


Figure 2

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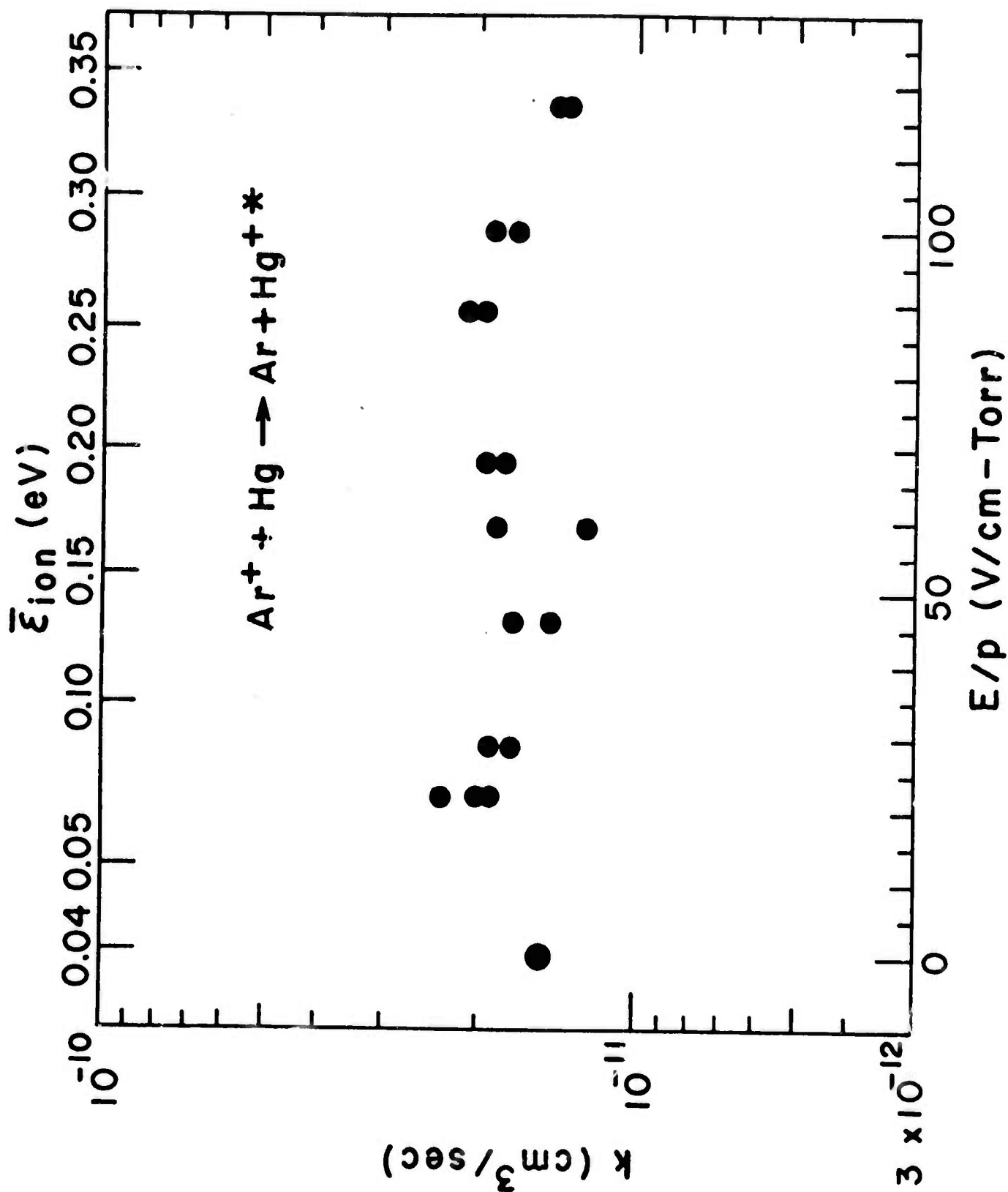


Figure 3